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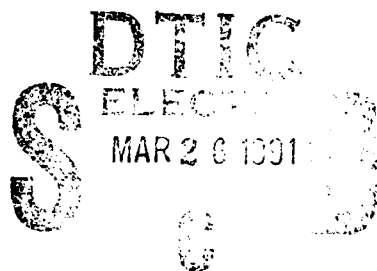
TECHNICAL REPORT BRL-TR-3212

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FOURIER TRANSFORM INFRARED SPECTROSCOPY
OF NITRIC OXIDE DURING EXPOSURE TO
VACUUM ULTRAVIOLET RADIATION

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MARCH 1991



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I. INTRODUCTION

The decomposition of energetic nitramines has been the subject of hundreds of articles over the past 50 years.¹ To our knowledge, however, there has been no investigation into the importance of molecular ions in the thermal degradation process. The ionization of NO when exposed to vacuum ultraviolet radiation has been well documented,² and is an appropriate starting point since NO has been observed as a product in thermal degradation studies on the nitramines RDX and HMX.³

We have designed and constructed an infrared spectral cell which fits in the bay of most standard FTIR spectrometers and enables the infrared spectrum of a gas to be collected while that gas is being exposed to the output of an electrodeless rare gas resonance lamp. The cell has been tested using nitric oxide as the gas which is exposed to the lamp output.

II. BACKGROUND

The spectrum of nitric oxide in the infrared and vacuum ultraviolet has been well characterized.²⁻⁵ The molecule is the simplest of the oxides of nitrogen, and has historical significance as the first diatomic to exhibit a Q-branch in the fundamental infrared absorption. Although much of what is known about the photochemistry of the oxides of nitrogen is due to their importance in understanding air pollution,⁴ to our knowledge, there has been no successful study of the gas phase spectroscopy of the nitrosyl ion, NO^+ .

III. EXPERIMENTAL

The vacuum ultraviolet-ir spectral cell apparatus is shown in Figure 1. The spectral cell consists of two equal length chambers in series, separated by a common window. All windows are of LiF. The total VUV-IR cell length is 15 centimeters. The first chamber is a microwave discharge flow lamp.⁶ The second chamber contains the gas whose IR spectrum is desired and may be operated as either a static or flow cell. It is necessary that the central window transmits vacuum ultraviolet and infrared radiation while it is sufficient for the outer two windows to transmit only in the infrared. Contained within this second chamber and out of the VUV light path are a pair of parallel plate electrodes, separated by 1.5 cm, which are used to monitor ion production at low plate voltages, or to increase ion production by accelerating photolytically produced electrons to ionizing potential energies at higher voltages. The infrared beam from the spectrophotometer is incident on and normal to the LiF window of the first chamber and is colinear with the cell cavity axis. Advantage is taken of the fact that the species in the first chamber (in this case D_2 in He because it was available) are transparent to infrared radiation.

The NO used in these experiments was chemically pure (C.P.) and was obtained from Matheson and used without further purification. Analysis of the gas by FTIR spectroscopy showed the main impurities to be NO_2 (~3%) and N_2O (~5%). The Deuterium-Helium mixture (0.1% D_2 in He) used in the microwave discharge lamp⁷ was

obtained from Spectra Gas Inc. Typical pressure in the microwave lamp was 2.3 torr with the flow rate adjusted to give maximum ion current across the parallel plate electrodes when a small (~ 1 V) potential was applied during irradiation of a few torr of NO. Microwave power was supplied by a Raytheon Physicians Diathermy Unit using a Broida-Evenson type cavity. The absence of a photoelectric effect was demonstrated by zero current flow during exposure of the evacuated IR chamber to the radiation at 121.5 nm while a small voltage was applied across the plates. At low sample gas pressures (~ 1 torr), ion current vs. voltage curves during exposure of nitric oxide to the VUV radiation agreed well with previous experiments performed on similar systems.⁸

The experimental procedure was as follows. A 0.1% D₂ in He gas mixture was allowed to flow through the lamp (left side in Figure 1) side of the cell. A needle valve upstream from the cell was used to adjust the flow of gas to give a reading of ~ 2.3 torr on an MKS Instruments capacitance manometer located between the needle valve and the cell. A Broida-Evenson microwave cavity was placed around the 13 mm quartz tubing on the lamp side of the cell. Using a Tesla coil, a 20 watt air cooled discharge was then initiated in the lamp side of the cell. With the sample side of the cell evacuated, a background spectrum was collected. The sample side of the cell was then filled with between 10 and 50 torr of NO. After one or two minutes, an IR spectrum of the gas was obtained, and ratioed against the background spectrum obtained previously. Spectra were collected and ratioed every 15 minutes, with the total exposure time always greater than 90 minutes. Exposure times longer than this produced only slight additional changes in products. No water or hydrocarbon peaks were observed in the spectra of any of the gas samples used in these experiments.

The quantities of NO, N₂O, and NO₂ in the right (sample) side of the cell during an experiment were determined using the integrated absorbance over the wavenumber regions, respectively, 1780-1960, 2125-2280, and 1500-1770. The integration region for NO₂ included the absorption regions for NO₂ and N₂O₄. At the low pressures used in these experiments, the N₂O₄ integrated absorbance was much smaller than the NO₂ integrated absorbance. No correction was made to account for differing oscillator strengths or mass balance between the equilibrium pair. Integrated absorbances were converted to pressures using a linear fit to integrated absorbance vs. pressure plots for pure samples of each gas in the discharge cell when no discharge was occurring. For these calibrations, the NO was the same as that used in these experiments. The NO₂ and N₂O were chemically pure and obtained from Matheson. No correction was made to account for contamination of the oxides of nitrogen by other oxides of nitrogen in the Beer's law

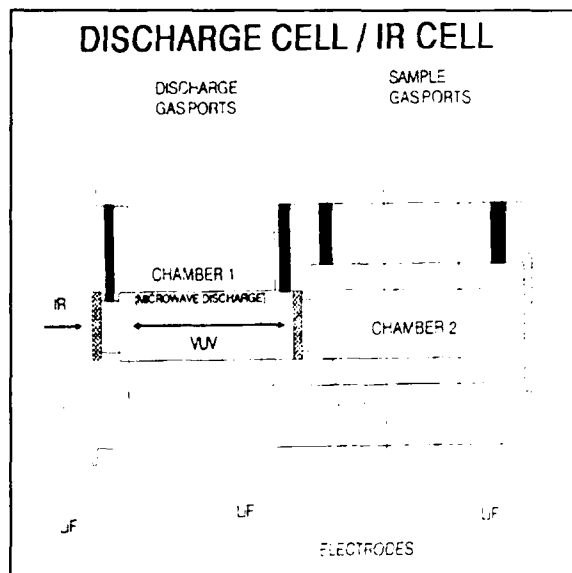


Figure 1. The Apparatus Used in These Experiments Which Enabled the Infrared Spectrum of a Gas to be Collected While that Gas was Being Exposed to Vacuum Ultraviolet Radiation

plots, even though these contaminants were present (evident from IR spectra) in small amounts in each gas sample.

The output of rare gas resonance lamps powered by microwave discharges has been shown to be of high intensity and purity.⁷ The resonance emission for Deuterium atoms occurs at 121.5 nm. To achieve maximum chromatic purity, it is necessary that the lamp be equipped with a getter to remove impurities, particularly water vapor, from the discharge gas. Our cell does not use a getter, so some error is introduced by assuming the output of the lamp to be monochromatic. No filter was used between the left (lamp) and right (sample) chambers of the cell to remove unwanted radiation.

IV. RESULTS AND DISCUSSION

Figure 2 shows a plot of integrated absorbance ($A \cdot \text{cm}^{-1}$) vs. time for NO, N_2O , and NO_2 when 15 torr of NO is exposed to the lamp output for 100 minutes. Figure 3 shows the experimental data reduced to pressure using the calibration curve for each oxide of nitrogen. The overall effect of exposure of the NO sample used in these experiments to radiation at 121.5 nm was decomposition of NO with subsequent formation of NO_2 . N_2O concentration decreased slightly throughout the course of the experiment.

Commercial grade NO always contains significant amounts of N_2O and NO_2 . Because of this, any model of the experiment described here must also take into account photolysis of N_2O and NO_2 .

The ionization potential and bond energy (D_0) for nitric oxide are 9.266 eV⁹ and 6.496 eV,¹⁰ respectively. Absorption of radiation at 121.5 nm by NO produces the nitrosyl ion,⁷ NO^+ :

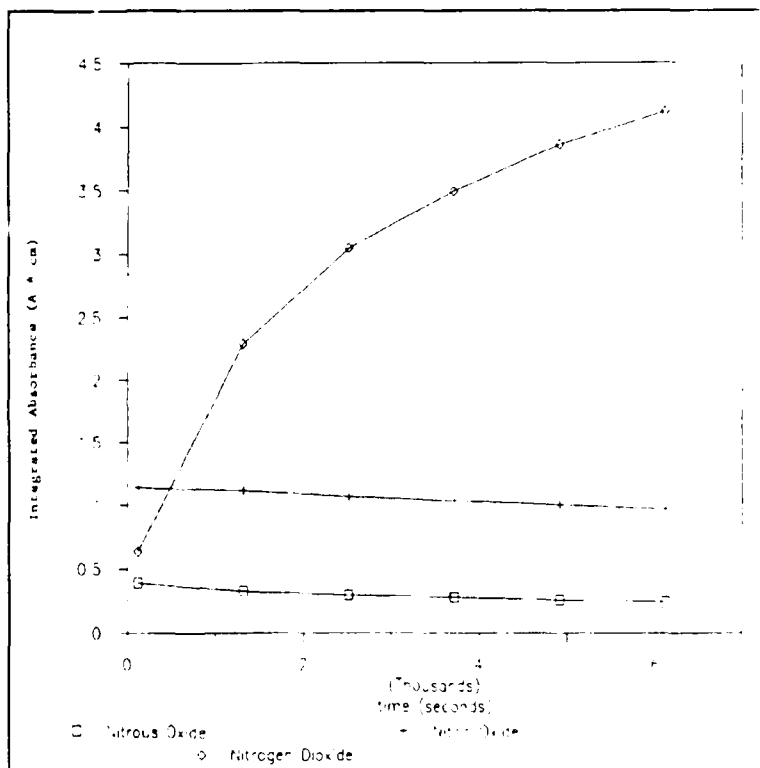


Figure 2. Integrated Absorbance Vs. Time Curves for the Gas Sample Used in this Experiment

The absorption coefficient at 121.5 nm is approximately $40 \text{ atm}^{-1} \text{ cm}^{-1}$. The photolysis of the nitric oxide was entered into the kinetic scheme as follows. Watanabe¹¹ has determined the photoionization cross section of NO at 121.6 nm to be approximately $10^{-18} \text{ cm}^2 \text{ mol}^{-1}$. In general,¹² electrodeless rare gas resonance lamps for photochemistry as used here have an output on the order of $10^{14} \text{ quanta cm}^{-2} \text{ sec}^{-1}$. The lamp used in these experiments is ungettered, so it is assumed that output is approximately decreased by an order of magnitude to $10^{13} \text{ quanta cm}^{-2} \text{ sec}^{-1}$. Since the lamp output is assumed to be constant, then:

$$[\text{NO}] = [\text{NO}_0] \exp(-kxt) \quad (2)$$

Since kx must have units of $1/\text{time}$, k must have units of

area. The area used is the photoionization cross section derived from Beer's law, yielding for these experiments an effective rate constant for NO ionization of 10^{-4} sec^{-1} . The gradient of nitrosyl ion concentration in the cell with respect to path length has not been considered.

At low pressures the main deactivation pathway of the nitrosyl ion is dissociative recombination⁸ to give N (^4S , ^2D) and O (^3P) atoms:



The rate constant for the recombination process (Eq. (3)) has been measured¹³ and found to be approximately equal to $1 \times 10^{16} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$.

For N_2O , the absorption coefficient at 121.5 nm is approximately¹⁴ $100 \text{ atm}^{-1} \text{ cm}^{-1}$. Bond dissociation energies are⁷ $D_0(\text{N}_2\text{-O}) = 1.67 \text{ eV}$ and $D_0(\text{N-NO}) = 4.99 \text{ eV}$. Photolysis of N_2O in the vacuum ultraviolet is not completely understood. Experimentally,¹² metastable species produced by photolysis of N_2O at wavelengths greater than 120 nm are O atoms (^1D , ^1S), N atoms (^2D , ^2P), and N_2 ($\text{B}^2\Pi$). At 123.6 nm, the ratio of quantum yields N_2/O_2 for N_2O photolysis is approximately 6. Products of photolysis of N_2O at 121.5 nm which are energetically possible are N_2 , NO, and N and O atoms, in their ground and excited state:

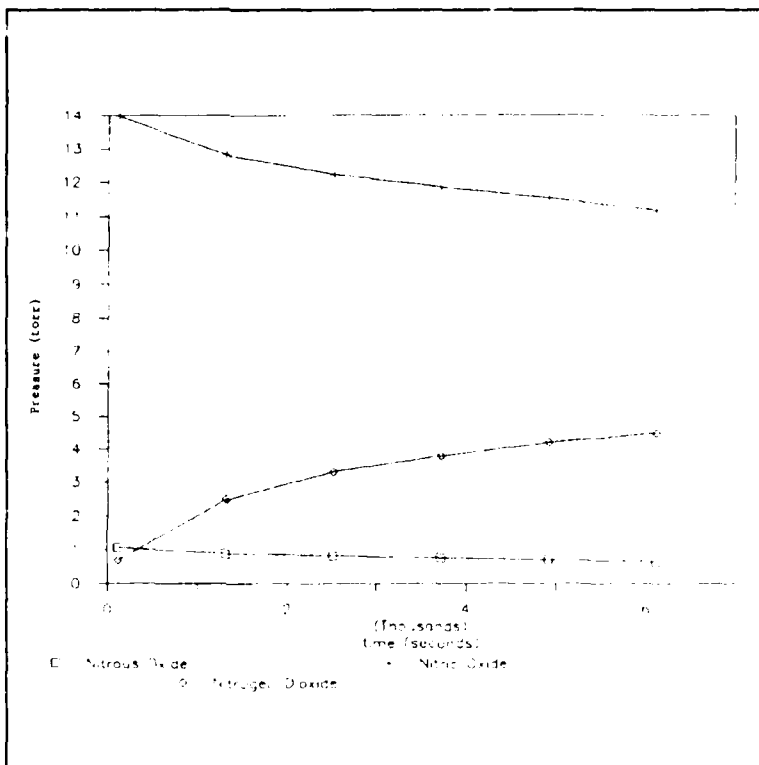


Figure 3. Pressure Vs. Time Curves for the Gas Sample Used in These Experiments. This graph was produced using pressure vs. absorbance curves for each oxide of nitrogen.



It was assumed that the effective rate constant for N_2O photolysis to give N_2 and O atoms was greater than the rate constant for NO photolysis by a factor equal to the ratio of the absorption coefficients for each oxide of nitrogen at 121.5 nm (approximately 2.5). For N_2O photolysis to give NO and N, the effective rate constant was made equal to one sixth of that for the photolysis which yields N_2 and O. The choice of this factor was somewhat arbitrary and based on the quantum yields mentioned above. It seems reasonable in light of the bond dissociation energies. Using the ratio of the bond dissociation energies instead of the quantum yield ratio had no apparent effect on the outcome of the kinetic calculation.

For NO_2 , the absorption coefficient at 121.5 nm is approximately⁷ $300 \text{ atm}^{-1}\text{cm}^{-1}$. The bond dissociation energy $D_0(\text{ON-O}) = 3.12 \text{ eV}$. Photodissociation in the vacuum ultraviolet produces NO ($A^2\Sigma^+ + B^2\Pi$) and O atoms ($^3P, ^1D$):



Similar to N_2O photolysis, the effective rate constant used for photolysis of NO_2 was increased over that for NO by a factor equal to the ratio of the absorption coefficients at 121.5 nm (7.5).

Table 1 shows the individual reactions which were assumed to be important for photolysis by radiation at 121.5 nm and subsequent reaction of the gas mixture used in these experiments. The set of simultaneous differential equations resulting from the reactions in Table 1 was solved using the ACUCHEM and ACUPLOT programs developed by Braun, Herron and Kahaner.¹⁵ Figure 4 shows the output of the ACUCHEM modeling program for the reactions listed in Table 1. The results of the ACUCHEM program and the experimental results agree to within the experimental error of the pressure calibration, which we believe to be within 10% of actual based on slight curvature of the Beer's law plots. The main

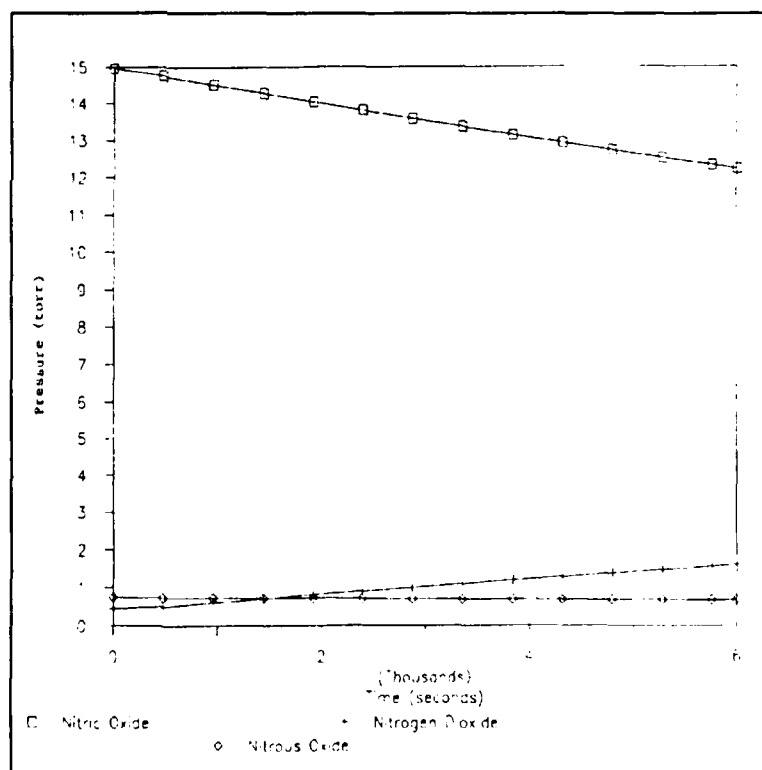


Figure 4. Output of the ACUCHEM Program Using Reactions from Table 1 for the Gas Sample During Exposure to Radiation at 121.5 nm

discrepancies between the experimental and calculated results are that in the experimental results the NO_2 concentration overtakes that of N_2O faster than that calculated using ACUCHEM and that the overall rate of disappearance of NO and appearance of NO_2 is faster experimentally than the calculated rate. This is probably due to the lamp output being slightly underestimated, since increasing the lamp output used in the ACUCHEM program by an order of magnitude moves the cross over point closer to that observed experimentally. Another source of the discrepancy may be that the lamp is emitting light at wavelengths other than 121.5 nm capable of photolyzing the sample gas. This has not been taken into account here. For the experiment reported here, spectra were collected at 4 cm^{-1} resolution for 250 scans. Scan time was 2 minutes 20 seconds. During the course of the experiment, the pressure in the cell increases a few percent, depending on initial pressure. We believe this is caused by heating from the discharge lamp. A stream of room temperature nitrogen is blown around the lamp during the experiment to minimize this effect. Figure 5 shows spectra from the beginning and end of a typical experiment. Depletion of NO and enrichment of NO_2 is evident, even without taking into account differing oscillator strengths in the infrared. Finally, we observed no evidence of NO disproportionation to N_2O and NO_2 as was recently reported in the literature.¹⁶

Table 1. Reactions Used as Input to the ACUCHEM Program

	Mechanism	Rate Constant at 300 K
a*	$\text{NO} = \text{NO}^+ + \text{e}$	$1 \times 10^{-4} \text{ sec}^{-1}$
b**	$\text{NO}^+ + \text{e} = \text{N} + \text{O}$	$1 \times 10^{16} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
c*	$\text{NO}_2 = \text{NO} + \text{O}$	$7.5 \times 10^{-5} \text{ sec}^{-1}$
d*	$\text{N}_2\text{O} = \text{N}_2 + \text{O}$	$2.5 \times 10^{-5} \text{ sec}^{-1}$
e*	$\text{N}_2\text{O} = \text{NO} + \text{N}$	$4.0 \times 10^{-6} \text{ sec}^{-1}$
f	$\text{NO} + \text{O} = \text{NO}_2$	$5 \times 10^7 \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
g	$\text{O} + \text{NO} + \text{M} = \text{NO}_2 + \text{M}$	$4.6 \times 10^{16} \text{ cm}^6\text{mole}^{-2}\text{sec}^{-1}$
h	$\text{NO} + \text{N} = \text{N}_2 + \text{O}$	$1.6 \times 10^{13} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
i	$\text{NO}_2 + \text{N} = \text{N}_2\text{O} + \text{O}$	$1.1 \times 10^{13} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
j	$\text{NO}_2 + \text{N} = \text{NO} + \text{NO}$	$3.6 \times 10^{12} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
k	$\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$	$3.68 \times 10^{12} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
l	$\text{O}_2 + \text{N} = \text{NO} + \text{O}$	$5.28 \times 10^7 \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
m	$\text{NO} + \text{NO} + \text{O}_2 = \text{NO}_2 + \text{NO}_2$	$7.2 \times 10^9 \text{ cm}^6\text{mole}^{-2}\text{sec}^{-1}$
n	$\text{O} + \text{O}_2 = \text{O}_3$	$2.0 \times 10^{14} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$
o	$\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$	$1.03 \times 10^{10} \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$

*Calculated in text.

**See Reference 13.

Unless otherwise indicated, all rate constants taken from:

D.L. Baulch, D.D. Drysdale, and D.G. Horne, "Evaluated Kinetic Data for High Temperature Reactions", CRC Press, Vol. 2, Cleveland, OH, 1973.

V. CONCLUSION

The combined rare gas resonance lamp - infrared cell has been used to monitor the effect of exposure of a sample of mixed oxides of nitrogen to radiation from a Deuterium atom resonance lamp. By assuming the output of the lamp to be monochromatic at 121.5 nm, a kinetic scheme has been devised which correctly predicts the behavior with time of the species being exposed to the lamp output. The electron-ion dissociative recombination mechanism for NO photolysis has been shown to account for the observed behavior of commercial grade NO during exposure to radiation at 121.5 nm. The development of the VUV-IR cell used in these experiments should enable the examination of infrared spectra of reacting chemical systems without the need for drastic modifications to conventional FTIR instrumentation.

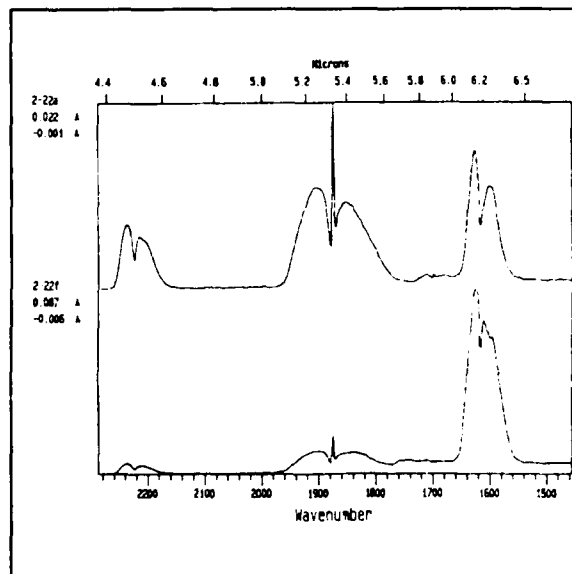


Figure 5. Infrared Spectra Corresponding to the First (Upper Spectrum) and Last (Lower Spectrum) Data Points in Figures 2 and 3. The spectra are not in scale to each other.

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